Dedicated to: Antonino Loiacono   Carmela Mazzuti

WEINHOLD'LENGTH IN AN ISOCHORIC THERMODYNAMIC SYSTEM WITH CONSTANT HEAT CAPACITY

MANUEL SANTORO

ABSTRACT. The purpose of this paper is to study thermodynamic length of an isochoric two dimensional thermodynamic system with constant heat capacity. We find that length is related to the heat flow into the substance. We give examples of Ideal gas and Van der Waals gas.

1. INTRODUCTION

Weinhold proposed a metric[12] η_{ij} in thermodynamic state space as second derivative of internal energy with respect to extensive variables X_i and X_j, namely $\eta_{ij} = \frac{\partial^2 U}{\partial X_i \partial X_j}$ with $i,j = 1,...,n$. Such a thermodynamic state space is the energy surface geometrically described by constitutive relation $U = U(X_1,...,X_n)$ where, for example, $X_1 = S$, $X_2 = V$,etc, with S and V being, respectively, the entropy and the volume of the thermodynamic system.

Weinhold metric was, then, considered by P. Salamon[5,6,7,8], R.S. Berry[5,7,8], J.Nulton[6,8], E. Ihrig[6], and others[7,9] to study the physical significance of thermodynamic length. It was found that the *local* meaning of η_{ij} is the distance[7] between the energy surface and the linear space tangent to this surface at some point where η_{ij} is evaluated. Indeed, consider a particular energy state denoted by coordinates $(X_1^0,...,X_n^0)$. The tangent space is attached to the energy surface at point $(U_0, X_1^0,...,X_n^0)$. Consider, now, a new energy state $(X_1,...,X_n)$ close enough to $(X_1^0,...,X_n^0)$. Then the distance between the point on the surface $(U, X_1,...,X_n)$ and the tangent space is the *availability*[5,7] or the available work[5] of the system. This is a local interpretation since it requires just small displacements, like for fluctuations, from the given point $(U_0, X_1^0,...,X_n^0)$ on the surface.

On the other hand, we could consider thermodynamic length taking the metric η_{ij} *globally*. With this approach, we look at a path ϕ on the energy surface between two states a_0 and a_1 and consider the length of the path

$$L_{a_0 a_1} = \int_{a_0}^{a_1} [\sum_{i,j} \eta_{ij} dX_i dX_j]^{\frac{1}{2}}$$

Such a length, in general, represents[7] the change in mean molecular velocity depending on the particular nature of the thermodynamic process defining the path ϕ and its dimension is square root of energy. But thermodynamic length was explicitly studied[7] just in the Ideal case. In particular, it was found that, for a reversible or endoreversible Ideal process at constant volume, thermodynamic length is given by[7]

$$L^v = 2\sqrt{C_v}[\sqrt{T_1} - \sqrt{T_0}] = \sqrt{\frac{\theta}{3}}[\sqrt{v_1^*} - \sqrt{v_0^*}]$$

where v_1^* and v_0^* are, respectively, the mean of the squares of the gas-kinetic velocities at T_1 and T_0, and $\theta = \frac{mC_v}{R}$, where m is the particle mass.

In this paper we shall generalize the physical interpretation of thermodynamic length to a two dimensional thermodynamic system with constant heat capacity and we shall see that length is strictly related to the concept of heat flux.

2. Thermodynamic length with Weinhold metric

The thermodynamic length between two points a_0 and a_1 in thermodynamic state space is given by the following equation

$$L_{a_0 a_1} = \int_{a_0}^{a_1} [\sum_{i,j} \eta_{ij} dX_i dX_j]^{\frac{1}{2}} \tag{2.1}$$

where η_{ij} are elements of the thermodynamic metric and X_i represent independent coordinates in thermodynamic state space. We are going to show that thermodynamic length in an isochoric thermodynamic system with two degrees of freedom with heat capacity constant is related to the heat flux of a quasi-static process at constant mole number.

In this manuscript, we shall give, first, a general discussion about thermodynamic length and, then, we shall focus our attention to the relation between length and heat flow.

Let's consider constitutive relation $u = u(s, v)$ where u is the molar internal energy, s is the molar entropy and v is the molar volume. s and v are the two independent variables. Then, it is known that Weinhold metric is given by[3]

$$\eta_{ij} = \frac{1}{c_v} \begin{pmatrix} T & -\frac{T\alpha}{k_T} \\ -\frac{T\alpha}{k_T} & \frac{c_p}{vk_T} \end{pmatrix} \tag{2.2}$$

where

(1) c_v is the molar heat capacity at constant volume:

$$c_v = T(\frac{\partial s}{\partial T})_v \quad ,$$

(2) c_p is the molar heat capacity at constant pressure:

$$c_p = T(\frac{\partial s}{\partial T})_p \quad ,$$

(3) α is the thermal coefficient of expansion:

$$\alpha = \frac{1}{v}(\frac{\partial v}{\partial T})_p \quad ,$$

(4) κ_T is the isothermal compressibility:

$$\kappa_T = -\frac{1}{v}(\frac{\partial v}{\partial p})_T \quad .$$

Thermodynamic length with such a metric is given by[7]

$$L = \int [\frac{T}{c_v}(ds)^2 - 2\frac{T\alpha}{c_v\kappa_T}dsdv + \frac{c_p}{vc_v\kappa_T}(dv)^2]^{\frac{1}{2}} \tag{2.3}$$

and, if molar entropy and molar volume are given parametrically as $s = s(\xi)$, $v = v(\xi)$, then we have[7]

$$L = \int_{\xi_i}^{\xi_f} [\frac{T}{c_v}(\frac{ds}{d\xi})^2 - 2\frac{T\alpha}{c_v\kappa_T}\frac{ds}{d\xi}\frac{dv}{d\xi} + \frac{c_p}{vc_v\kappa_T}(\frac{dv}{d\xi})^2]^{\frac{1}{2}}d\xi \tag{2.4}$$

Our study is going to focus on length at constant volume which is given by[9]

$$L^v = \int \sqrt{\frac{T}{c_v}}ds = \int \sqrt{\eta_{11}}ds \tag{2.5}$$

3. Thermodynamic length in an isochoric TD system with constant heat capacity

3.1. General discussion. Consider constant molar heat capacity at constant volume $c_v = T(\frac{\partial s}{\partial T})_v$. Then $(\frac{\partial T}{\partial s})_v = \frac{T}{c_v}$ and since $T = (\frac{\partial u}{\partial s})_v$, we get the following equation[11]

$$\frac{\partial^2 u}{\partial s^2} - \frac{1}{c_v}\frac{\partial u}{\partial s} = 0. \tag{3.1}$$

Integrating once we get

$$\frac{\partial u}{\partial s} = \frac{u}{c_v} + f_2(v),$$

with an arbitrary function $f_2(v)$. Solving this equation we get the fundamental constitutive law in the form[11]

$$u(s,v) = f_1(v)e^{\frac{s-s_0}{c_v}} - c_v f_2(v), \tag{3.2}$$

with another arbitrary function $f_1(v)$.

Example 1. Ideal Gas

It is known[1] that for an Ideal Gas

$$s = s_0 + c_v \ln\left(\frac{u}{u_0}\right) + R\ln\left(\frac{v}{v_0}\right)$$

Let $u_0 = v_0 = 1$ for simplicity. Then, solving for the internal energy, we get

$$u = v^{-\frac{R}{c_v}} e^{\frac{s-s_0}{c_v}} \tag{3.3}$$

Therefore, considering (3.2), we get the Ideal Gas case if we set $f_1(v) = v^{-\frac{R}{c_v}}$ and $f_2(v) = 0$.[11]

Example 2. Van der Waals Gas

The entropy function of the Van der Waals Gas is given by[1]

$$s = s_0 + R\ln\left[(v-b)(u+\frac{a}{v})^{\frac{c_v}{R}}\right]$$

where a and b are positive constants.

Then, solving for u, we get

$$u = (v-b)^{-\frac{R}{c_v}} e^{\frac{s-s_0}{c_v}} - \frac{a}{v} \tag{3.4}$$

Therefore, considering the general case with heat capacity constant (3.2), we get the Van der Waals Gas case if we set $f_1(v) = (v - b)^{-\frac{R}{c_v}}$ and $f_2(v) = \frac{a}{c_v v}$.[11]

We have realized, so far, that equation (3.2) is very general as long as heat capacity is constant. Therefore, our first goal is to try to express thermodynamic length at constant volume in the same way.

Considering (2.5), we have the following relation

$$\frac{\partial^2 L^v}{\partial s^2} = \frac{1}{2c_v}\frac{\partial L^v}{\partial s} \tag{3.5}$$

Integrating once we get

$$\frac{\partial L^v}{\partial s} = \frac{L^v}{2c_v} + h_2(v)$$

where $h_2(v)$ is some arbitrary function of v.

Integrating once more we get the interesting result

$$L^v = 2[h_1(v)e^{\frac{s-s_0}{2c_v}} - c_v h_2(v)] \tag{3.6}$$

with $h_1(v)$ also arbitrary function.

In this case, h_1 and h_2 are completely unknown functions of molar volume. Nevertheless, we can still recover some information just about h_1 in the following way.

Since

$$T = (\frac{\partial u}{\partial s})_v = \frac{u}{c_v} + f_2(v)$$

then, it is easy to see that $\frac{T}{c_v} = \frac{f_1(v)}{c_v^2}e^{\frac{s-s_0}{c_v}}$ and , therefore,

$$\sqrt{\frac{T}{c_v}} = \frac{\sqrt{f_1(v)}}{c_v}e^{\frac{s-s_0}{2c_v}} \tag{3.7}$$

This implies that thermodynamic length at constant volume is given by

$$L^v = \frac{\sqrt{f_1(v)}}{c_v}\int e^{\frac{s-s_0}{2c_v}}ds = 2\sqrt{f_1(v)}e^{\frac{s-s_0}{2c_v}} + k(v) \tag{3.8}$$

where $k(v)$ is any function of the molar volume.

This result implies that h_1 is known for specific examples being $h_1(v) = \sqrt{f_1(v)}$, while h_2 is not. Therefore, we exactly know what thermodynamic length of a two dimensional isochoric system at constant heat capacity is up to a constant.

Let's rewrite thermodynamic length in the following way by setting $k(v) = -2c_v h_2(v)$,

$$L^v = 2[\sqrt{f_1(v)}e^{\frac{s-s_0}{2c_v}} - c_v h_2(v)] \tag{3.9}$$

Remark 1. It seems reasonable to think that h_2 would be somehow related to f_2 as h_1 is to f_1. But, at this point, such a statement cannot be made.

Now, since for an isochoric system $dq = du = Tds = \frac{f_1(v)}{c_v}e^{\frac{s-s_0}{c_v}}ds$, where dq is the infinitesimal heat or heat flux per unit mole, then we have the following result

Lemma 1.

$$\left(\frac{dL^v}{ds}\right)^2 = \frac{1}{c_v}\frac{dq}{ds} \tag{3.10}$$

3.2. **Relation between "isochoric" length and heat.** Here we'll derive a relation between the heat flux q as difference in molar internal energy and thermodynamic length of a quasi-static isochoric process.

Since the molar volume is constant, consider $u_2 = u(s_2, v)$ and $u_1 = u(s_1, v)$. Let both s_1 and s_2 being greater than the initial entropy s_0. It is important to realize that conditions on the molar entropy s are equivalent to conditions on the temperature since $T = \frac{f_1(v)}{c_v}e^{\frac{s-s_0}{c_v}}$ with both heat capacity and volume constant. Since $q = \Delta u = u_2 - u_1$, then, considering (3.2), we have

$$q = u_2 - u_1 = f_1(v)[e^{\frac{s_2-s_0}{c_v}} - e^{\frac{s_1-s_0}{c_v}}] = c_v(T_2 - T_1) \tag{3.11}$$

with the mass of the substance normalized to 1.

Similarly, considering the general expression of thermodynamic length (3.9) we have

$$L^v = 2\sqrt{f_1(v)}[e^{\frac{s_2-s_0}{2c_v}} - e^{\frac{s_1-s_0}{2c_v}}] \tag{3.12}$$

Let's set $s_1 < s_2$ or, equivalently, $T_1 < T_2$. Then, requiring length to be always positive or equal to zero, we will consider

$$1)L^v = \int_{s_1}^{s_2} \sqrt{\frac{T}{c_v}} ds$$

$$2) - L^v = \int_{s_2}^{s_1} \sqrt{\frac{T}{c_v}} ds$$

Let's now, for simplicity, set $s_0 = s_1$. Then we can rewrite both equations (3.11) and (3.12) in the following way

$$q_{in} = f_1(v)[e^{\frac{s_2-s_1}{c_v}} - 1] > 0 \qquad q_{out} = f_1(v)[1 - e^{\frac{s_2-s_1}{c_v}}] < 0 \qquad (3.13)$$

and

$$L^v = 2\sqrt{f_1(v)}[e^{\frac{s_2-s_1}{2c_v}} - 1] \qquad -L^v = 2\sqrt{f_1(v)}[1 - e^{\frac{s_2-s_1}{2c_v}}] \qquad (3.14)$$

From these important expression of heat and length it follows,

Theorem 1.

$$q_{in} = \frac{L^v}{4}[L^v + 4\sqrt{f_1(v)}] \qquad (3.15)$$

or, equivalently,

$$(L^v)^2 + 4\sqrt{f_1(v)}L^v - 4q_{in} = 0 \qquad (3.16)$$

It easily follows that

$$q_{out} = -q_{in} = \frac{-L^v}{4}[L^v + 4\sqrt{f_1(v)}] \qquad (3.17)$$

or, equivalently,

$$(L^v)^2 + 4\sqrt{f_1(v)}L^v + 4q_{out} = 0 \qquad (3.18)$$

We also have the following two corollaries,

Corollary 1.

$$L^v = 2[\sqrt{f_1(v) + q_{in}} - \sqrt{f_1(v)}] = 2[\sqrt{u_2} - \sqrt{u_1}] \qquad (3.19)$$

which is equivalent to

$$-L^v = 2[\sqrt{f_1(v)} - \sqrt{f_1(v) - q_{out}}] = 2[\sqrt{u_1} - \sqrt{u_2}] \tag{3.20}$$

Corollary 2.

$$\pm L^v = 0 \qquad iff \qquad q = 0 \tag{3.21}$$

Considering equation (3.11), $q = 0$ iff $T_2 = T_1$. Therefore, it does make sense that, at thermal equilibrium, thermodynamic length $L^v = 0$.

4. Examples

4.1. **Ideal Gas.** In example 1, we have seen that $f_1(v) = v^{-\frac{R}{c_v}}$. Therefore,

$$L^v = 2[\sqrt{v^{-\frac{R}{c_v}} + q_{in}} - \sqrt{v^{-\frac{R}{c_v}}}] \tag{4.1}$$

or

$$-L^v = 2[\sqrt{v^{-\frac{R}{c_v}}} - \sqrt{v^{-\frac{R}{c_v}} - q_{out}}] \tag{4.2}$$

4.2. **Van der Waals Gas.** In case of Van der Waals gas, we have shown in example 2 that $f_1(v) = (v - b)^{-\frac{R}{c_v}}$. Therefore,

$$L^v = 2[\sqrt{(v - b)^{-\frac{R}{c_v}} + q_{in}} - \sqrt{(v - b)^{-\frac{R}{c_v}}}] \tag{4.3}$$

or

$$-L^v = 2[\sqrt{(v - b)^{-\frac{R}{c_v}}} - \sqrt{(v - b)^{-\frac{R}{c_v}} - q_{out}}] \tag{4.4}$$

5. Conclusions

We have tried to achieve a physical interpretation of thermodynamic length in a simple isochoric thermodynamic system with two degree of freedom with constant heat capacity. We also gave examples like Ideal Gas and Van der Waals Gas.

6. Comments

I am aware of the fact that reference [11] has not been submitted yet. But all the steps needed to the reader for a full understanding are entirely reported.

References

[1] H.B. Callen, *Thermodynamics*, Whiley, 1960.

[2] L. Diosi, K. Kulacsy, B. Lukacs, A. Racz, *Thermodynamic length, time, speed and optimum path to minimize entropy production*, arXiv:cond-mat/9503174, 1995.

[3] R. Mrugala, *On equivalence of two metrics in classical thermodynamics*, Physica A, v.125, 631-639, 1984.

[4] G. Ruppeiner, *Thermodynamics: A Riemannian geometric model* Phys. Rev. A, 20(4), 1608-1613, 1979.

[5] P. Salamon, R.S. Berry, *Thermodynamic Length and Dissipated Availability*, Phys. Rev. Lett., v.51(13), 1127-1130, 1983.

[6] P. Salamon, J. Nulton, E. Ihrig, *On the relation between entropy and energy versions of thermodynamics length*, J.Chem.Phys., v.80, 436, 1984.

[7] P. Salamon, B. Andresen, P.D. Gait, R.S. Berry, *The significance of Weinhold's length* J.Chem.Phys., v.73(2), 1001-1002, 1980.

[8] P. Salamon, J.D. Nulton, R.S. Berry, *Length in statistical thermodynamics* J.Chem.Phys., v.82(5), 2433-2436, 1985.

[9] M. Santoro, *Thermodynamic length in a two-dimensional thermodynamic state space*, J.Chem.Phys., v.121, n.7, pp.2932-2936., 2004.

[10] M. Santoro, *On the Helmholtz Potential metric: The Isotherm Length-Work Theorem*, arXiv,org, math-ph/0404040.

[11] M. Santoro, S. Preston, *Curvature of the Weinhold metric for thermodynamical systems with 2 degrees of freedom*, manuscript to be submitted .

[12] F. Weinhold, *Metric Geometry of equilibrium thermodynamics* p.I-V, J.Chem. Phys., v.63, n.6, 2479-2483, 2484-2487, 2488-2495, 2496-2501, 1976, v.65, n.2, pp.559-564, 1976.

Department of Mathematics and Statistics, Portland State University, PO Box 751, Portland, OR 97207-0751, USA

E-mail address: emanus@pdx.edu